# Hydrous ruthenium oxide supported on $Co_3O_4$ as efficient catalyst for aerobic oxidation of amines

**Feng Li, Jing Chen, Qinghong Zhang and Ye Wang***

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Ruthenium catalysts supported on various metal oxides and $Co_3O_4$-supported various transition metal catalysts prepared by an adsorption-precipitation method were examined for the aerobic oxidation of benzyl amine. We found that the $Co_3O_4$-supported ruthenium catalyst exhibited the best catalytic performance. The $Co_3O_4$-supported ruthenium catalyst was also effective for the aerobic oxidation of several other amines. The present catalyst could be used recyclably and be operated under solvent-free conditions. The activity of the present catalyst for the aerobic oxidation of benzyl amine depended less on the oxygen pressure, and the catalyst was also efficient even when air was used as an oxidant. The content of ruthenium and the size of $Co_3O_4$ particles played crucial roles in determining the catalytic performance. We have clarified that the supported hydrous ruthenium oxide ($RuO_2{\cdot}xH_2O$) is the active species for the aerobic oxidation of benzyl amine, whereas the supported metallic ruthenium (Ru°) and supported ruthenium chloride ($RuCl_3$) are inactive, and the supported anhydrous ruthenium oxide ($RuO_2$) only exhibits a lower activity.



## Introduction

Many oxidative transformations of organic compounds are currently still carried out using stoichiometric amounts of metal-based oxidants such as dichromate, permanganate and silver oxide, and large amounts of heavy metal salts are produced.[1] Selective oxidation of organic compounds by a catalytic method using $O_2$ or air as a sole oxidant has become urgent from the viewpoints of green chemistry.[2] Nitriles are important and versatile synthetic intermediates. As compared with the current production methods such as the nucleophilic substitution of halides with cyanide ions, the ammoxidation and the oxidation of amines with stoichiometric regents, the catalytic oxidation of primary amines by $O_2$ or air is a more desirable route for the synthesis of nitriles. However, only limited catalytic systems have been reported for the selective oxidation of amines by $O_2$.[3–11]

We have focused on the development of efficient heterogeneous catalysts for the selective oxidation of amines by $O_2$ or air because heterogeneous catalysts possess obvious advantages in product isolation and catalyst recycling uses than homogeneous catalysts. Although a large number of heterogeneous catalysts have been reported for the selective oxidation of alcohols, only very few studies have been contributed to the oxidation of amines over a heterogeneous catalyst.[7,8,11] A Ru/hydroxyapatite could catalyze the aerobic oxidation of several primary amines to the corresponding nitriles with good efficiencies.[7] For example, the conversion and selectivity for the oxidation of benzyl amine to benzonitrile were 100% and 90%, respectively, after a reaction at 383 K for 12 h over this catalyst, giving a turnover frequency (TOF) of ~0.5 $h^{-1}$.[7] Yamaguchi and Mizuno[8] reported that $Ru/Al_2O_3$ was more active for the aerobic oxidation of amines; the conversion of benzyl amine was >99% after 1 h of reaction at 373 K, providing a TOF of ~29 $h^{-1}$, but the selectivity of benzonitrile was lower (82%). Recently, a $Ru/Fe_3O_4$ was also reported to show good activity for the aerobic oxidation of amines, and the conversion and selectivity for the oxidation of benzyl amine to benzonitrile were 96% and 82%, respectively, after a 7 h reaction at 378 K, showing a TOF of ~3 $h^{-1}$.[11]

Recently, we examined the catalytic performances of ruthenium catalysts loaded on various metal oxide supports and various transition metal catalysts supported on $Co_3O_4$ for the aerobic oxidation of benzyl amine. We found that the $Co_3O_4$-supported ruthenium catalyst prepared by an adsorption-precipitation method exhibited outstanding catalytic performances. The present paper reports the catalytic behaviour of the $Co_3O_4$-supported ruthenium catalyst for the aerobic oxidation of amines. Catalyst requirements for this green oxidation and the nature of the active ruthenium species are also discussed *via* investigations of structure-reactivity relationships.

## Experimental

### Catalyst preparation

The catalysts used in the present work were mainly prepared by an adsorption-precipitation method. As an example, the procedure for the preparation of the $Co_3O_4$-supported ruthenium catalyst was described as follows. Powdery $Co_3O_4$ (1 g), purchased from the Sinopharm Group Chemical Reagent Co., was added into an aqueous solution of $RuCl_3$ (30 $cm^3$), and the

*State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China. E-mail: wangye@xmu.edu.cn; Fax: +86-592-2183047; Tel: +86-592-2186156*

**Table 1** Preparation procedures for $Co_3O_4$-supported ruthenium catalysts possibly with ruthenium in different states

| Catalyst denotation | Preparation procedure | Surf. area ($m^2\ g^{-1}$) |
|---|---|---|
| 2.5 wt% $Ru/Co_3O_4$ | Adsorption-precipitation method | 32 |
| 2.5 wt% $Ru/Co_3O_4$–C573 | Calcination of the 2.5 wt% $Ru/Co_3O_4$ in air at 573 K for 6 h | 29 |
| 2.5 wt% $Ru/Co_3O_4$–C573-R623 | Reduction of the 2.5 wt% $Ru/Co_3O_4$–C573 in $H_2$ at 623 K for 2 h | 13 |
| 3 wt% $Ru/Co_3O_4$ (*imp*) | Impregnation of $Co_3O_4$ with a $RuCl_3$ aqueous solution, followed by drying at 373 K | 26 |
| 3 wt% $Ru/Co_3O_4$ (*imp*)–C573 | Calcination of the 3 wt% $Ru/Co_3O_4$ (*imp*) in air at 573 K for 6 h | 30 |

concentration of $RuCl_3$ was used to regulate the Ru content. After the suspension was stirred at room temperature for 1 h, the pH was adjusted to 13.0 using 1 M NaOH aqueous solution. The solid powder obtained was recovered by filtration after the suspension was further stirred for 1 h. Subsequently, the solid powder was washed thoroughly with deionised water until $Cl^-$ was removed. The sample was washed further with ethanol, and was finally dried at room temperature (~298 K) in vacuum. The catalyst prepared by this adsorption-precipitation method was denoted as *m* wt% $Ru/Co_3O_4$, where *m* was the weight percentage of ruthenium. It should be noted that this denotation does not mean that ruthenium is in metallic (Ru°) state. For comparison, $Co_3O_4$ purchased from Alfa Aesar Co. (denoted as $Co_3O_4$-*A*) was also used for the preparation of a 2.5 wt% $Ru/Co_3O_4$-*A* catalyst by the same procedure. We clarified that the mean size of the $Co_3O_4$-*A* particles was larger than that of the $Co_3O_4$ particles purchased from the Sinopharm Group Chemical Reagent Co.

To gain information about the state of ruthenium in active catalysts, we also prepared $Co_3O_4$-supported ruthenium catalysts possibly with ruthenium in different states by different procedures as summarized in Table 1. The catalyst denoted as 2.5 wt% $Ru/Co_3O_4$–C573 was obtained by calcination of the 2.5 wt% $Ru/Co_3O_4$ catalyst prepared above with the adsorption-precipitation method at 573 K in air for 6 h. The 2.5 wt% $Ru/Co_3O_4$–C573-R623 denotes the catalyst obtained by further reduction of the 2.5 wt% $Ru/Co_3O_4$–C573 sample at 623 K in a $H_2$ gas flow for 2 h. The catalyst denoted as 3 wt% $Ru/Co_3O_4$ (*imp*) was prepared by an impregnation method as follows. Powdery $Co_3O_4$ (1 g) was added into the aqueous solution of $RuCl_3$ (30 $cm^3$) with a fixed concentration. The suspension was stirred for 4 h and was then allowed to rest overnight at ambient temperature. Subsequently, the mixture was evaporated to dryness at 343 K with continuous stirring, followed by further drying in air at 373 K to obtain the 3 wt% $Ru/Co_3O_4$ (*imp*). The 3 wt% $Ru/Co_3O_4$ (*imp*) was calcined in air at 573 K for 6 h, giving the sample denoted as 3 wt% $Ru/Co_3O_4$ (*imp*)-C573.

### Catalyst characterization

The content of ruthenium in each sample was determined by inductively coupled plasma (ICP) optical emission spectrometry using an Agilent ICP-MS 4500–300. The BET surface areas were measured with a high-speed automated area and pore size analyzer (Quantachrome NOVA 4000e). X-ray diffraction (XRD) patterns of the catalysts were measured with a Panalytical X′Pert Pro Super X-ray diffractometer equipped with X′Celerator detection systems. Cu $K_\alpha$ radiation (40 kV and 30 mA) was used as the X-ray source. Scanning electron microscopy (SEM) was carried out using a LEO1530 scanning electron microscope with 20 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) was measured with a PHI Quantum 2000 Scanning ESCA Microprobe equipment using monochromatic Al $K_\alpha$ radiation. $H_2$ temperature-programmed reduction ($H_2$-TPR) was performed using a Micromeritics AutoChem 2920 II instrument. Typically, the temperature of the sample loaded in a quartz reactor was raised to 1200 K in a $H_2$-Ar gas mixture (10 vol% $H_2$) at a rate of 10 K $min^{-1}$. The consumption of $H_2$ was monitored by a thermal conductivity detector, and the detector response was calibrated using the reduction of CuO powder.

### Catalytic reaction

The selective oxidation of amines with $O_2$ or air was carried out using a round-bottomed glass flask reactor equipped with a reflux condenser. In a typical run, a measured amount of catalyst (typically, 0.1 g) was added to the reactor pre-charged with desired amounts of reactant and solvent at a fixed temperature (typically, 373 K). Trifluorotoluene ($PhCF_3$), a stable and versatile solvent with relatively higher boiling point (375K) and lower toxicity as compared with many other organic solvents such as benzene and dichloromethane,[12] was used as the solvent in most of our experiments. The inhalation and direct contacts of $PhCF_3$ with the skin or eyes should be avoided because its toxicological properties have not been thoroughly investigated. The reaction was started by bubbling $O_2$ or $O_2$ diluted with $N_2$ or air into the liquid. The reactant mixture was stirred vigorously during the reaction. After the reaction, the catalyst was filtered off *via* centrifugation, and the liquid organic products were quantified by a gas chromatograph (Shimadzu 14B) equipped with a capillary column (DB-5, 30 M × 0.25 mm × 0.25 μm) and a FID detector using hexane as an internal standard. The turnover frequency (TOF) was calculated by the moles of amines converted per mole of ruthenium contained in the catalyst per hour.

## Results and discussion

### Superior catalytic performance of $Ru/Co_3O_4$ catalyst for the aerobic oxidation of benzyl amine

Only very limited heterogeneous catalysts have been reported for the aerobic oxidation of amines, and ruthenium has been exploited as the active component in all of these catalysts.[7,8,11] However, different supports were employed in different studies. Thus, we first examined the most suitable catalyst support. Table 2 shows the catalytic performances of ruthenium catalysts supported on various inorganic supports prepared by the adsorption-precipitation method. Under the



**Table 2** Catalytic behaviours of various metal oxide-supported Ru catalysts for aerobic oxidation of benzyl amine to benzonitrile[a]

| Entry | Catalyst | Surf. area ($m^2$ $g^{-1}$) | Conv. (%) | Select. (%) |
|---|---|---|---|---|
| 1 | None | — | <0.1 | — |
| 2 | $Ru/SiO_2$ | 6.3 | 21 | >99 |
| 3 | $Ru/Al_2O_3$ | 245 | 54 | >99 |
| 4 | $Ru/ZrO_2$ | 17 | 36 | >99 |
| 5 | Ru/SBA-15 | 324 | 29 | >99 |
| 6 | $Ru/CeO_2$ | 8.7 | 34 | >99 |
| 7 | $Ru/Pb_3O_4$ | 8.5 | 11 | >99 |
| 8 | $Ru/MnO_2$ | 3.7 | 26 | >99 |
| 9 | $Ru/Fe_2O_3$ | 10 | 35 | >99 |
| 10 | $Ru/Fe_3O_4$ | 47 | 30 | >99 |
| 11 | Ru/CoO | 7.2 | 43 | >99 |
| 12 | $Ru/Co_3O_4$ | 32 | 95 | >99 |
| 13 | Ru/ZnO | 12 | 15 | >99 |
| 14 | Ru/hydrotalcite | 41 | 35 | >99 |
| 15 | Ru/hydroxyapatite | 78 | 83 | 70 |

[a] Reaction conditions: Ru content, 3.0 wt% for all of the catalysts except for the $Ru/Co_3O_4$, which has a Ru content of 2.5 wt%; catalyst amount, 0.1 g; benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K; time, 1 h.

reaction conditions shown in Table 2, all of these catalysts except for the Ru/hydroxyapatite exhibited good selectivity for the formation of benzonitrile from benzyl amine. Although the Ru/hydroxyapatite showed a relatively higher conversion of benzyl amine (entry 15), this catalyst produced *N*-benzylidenebenzylamine as a main by-product with a considerable selectivity. This is different from the result reported for the hydroxyapatite-immobilized monomeric $Ru^{III}$ catalyst prepared by an ion-exchange method, where a higher selectivity could be obtained.[7] This may imply that different states of ruthenium exhibit different catalytic properties. The BET surface area of each sample is also shown in Table 2. It can be seen that there is no definite correlation between the activity and the BET surface area for the catalysts with different kinds of supports. Thus, the chemical nature of the support may play a key role in determining the catalytic performance. Among various supported ruthenium catalysts we examined, the $Ru/Co_3O_4$ showed the best catalytic performance for the aerobic oxidation of benzyl amine to benzonitrile (entry 12). Benzyl amine conversion and benzonitrile selectivity were 95 and >99%, respectively. The present $Ru/Co_3O_4$ catalyst provided a TOF of 38 $h^{-1}$ at 373 K for the conversion of benzyl amine based on Ru, which was significantly higher than those reported for the Ru/hydroxyapatite and the $Ru/Fe_3O_4$ catalysts.[7,11] This TOF value was slightly higher than that reported for the $Ru/Al_2O_3$ catalyst.[8] We also examined the catalytic performance of $Ru/Al_2O_3$ (entry 3), and it showed a relatively higher activity than other supported Ru catalysts except for the $Ru/Co_3O_4$ and the Ru/hydroxyapatite in our case.

Subsequently, we tested $Co_3O_4$-supported various transition metal catalysts for the aerobic oxidation of benzyl amine. The catalytic performances over these catalysts prepared by the adsorption-precipitation method are summarized in Table 3. Over these catalysts, the selectivity to benzonitrile was always >99%. However, only the $Ru/Co_3O_4$ catalyst exhibited a considerable benzyl amine conversion. Other catalysts could not provide benzyl amine conversions significantly higher than $Co_3O_4$ alone. Thus, ruthenium was a very unique active component and $Co_3O_4$ was a superior catalyst support for the aerobic oxidation of benzyl amine to benzonitrile.

**Table 3** Catalytic behaviours of $Co_3O_4$-supported various transition metal catalysts for aerobic oxidation of benzyl amine to benzonitrile[a]

| Entry | Catalyst[b] | Conversion (%) | Selectivity (%) |
|---|---|---|---|
| 1 | $Co_3O_4$ | 2.0 | >99 |
| 2 | $Au/Co_3O_4$ | 1.0 | >99 |
| 3 | $Pd/Co_3O_4$ | 1.4 | >99 |
| 4 | $Rh/Co_3O_4$ | 0.8 | >99 |
| 5 | $Pt/Co_3O_4$ | 1.0 | >99 |
| 6 | $Ru/Co_3O_4$ | 95 | >99 |
| 7 | $Cu/Co_3O_4$ | 1.5 | >99 |
| 8 | $Co/Co_3O_4$ | 0.6 | >99 |
| 9 | $Fe/Co_3O_4$ | 0.2 | >99 |
| 10 | $Ni/Co_3O_4$ | 0.7 | >99 |
| 11 | $Ir/Co_3O_4$ | 0.9 | >99 |

[a] Reaction conditions: metal content, 3.0 wt% for all of the catalysts except for the $Ru/Co_3O_4$, which has a Ru content of 2.5 wt%; catalyst amount, 0.1 g; benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K; time, 1 h. [b] All of the supported catalysts were prepared by the adsorption-precipitation method, and the metal precursors were $AuCl_3$, $PdCl_2$, $RhCl_3$, $PtCl_2$, $RuCl_3$, $Cu(NO_3)_2$, $Co(NO_3)_2$, $Fe(NO_3)_3$, $Ni(NO_3)_2$ and $IrCl_3$ for the catalysts used for entries 2–11, respectively.

### Effects of Ru content and $Co_3O_4$ size of $Ru/Co_3O_4$ catalysts on their catalytic performances for aerobic oxidation of benzyl amine

Table 4 shows the effect of Ru loadings on catalytic properties of the $Ru/Co_3O_4$ catalysts prepared by the adsorption-precipitation method. At a fixed amount of catalyst (0.1 g, entries 1–6), benzyl amine conversion increased with increasing Ru content up to 2.5 wt%, and a further increase in Ru content from 2.5 to 3.5 wt% decreased benzyl amine conversion. Comparisons at a fixed amount of Ru (9.8 μmol, entries 7–11) by regulating the catalyst amount showed that the conversion of benzyl amine decreased monotonically with a rise in Ru content. Especially, a sharp decrease was observed as Ru content was raised from 2.5 to 3.5 wt%. This significant drop in catalytic activity at higher Ru contents may imply that only the ruthenium species highly dispersed on $Co_3O_4$ or intimately contacted with $Co_3O_4$ particles are active for the aerobic oxidation of benzyl amine.

**Table 4** Catalytic behaviours of $Ru/Co_3O_4$ catalysts with different Ru contents or different sizes of $Co_3O_4$ for aerobic oxidation of benzyl amine to benzonitrile[a]

| Entry | Catalyst | Ru amount (μmol) | Conv. (%) | Select. (%) |
|---|---|---|---|---|
| 1[b] | $Co_3O_4$ | — | 2.0 | >99 |
| 2[b] | 1.0 wt% $Ru/Co_3O_4$ | 9.8 | 61 | >99 |
| 3[b] | 1.7 wt% $Ru/Co_3O_4$ | 16.8 | 83 | >99 |
| 4[b] | 2.5 wt% $Ru/Co_3O_4$ | 24.7 | 95 | >99 |
| 5[b] | 3.5 wt% $Ru/Co_3O_4$ | 34.6 | 75 | >99 |
| 6[b] | 10 wt% $Ru/Co_3O_4$ | 98.9 | 70 | >99 |
| 7[c] | 1.0 wt% $Ru/Co_3O_4$ | 9.8 | 61 | >99 |
| 8[c] | 1.7 wt% $Ru/Co_3O_4$ | 9.8 | 43 | >99 |
| 9[c] | 2.5 wt% $Ru/Co_3O_4$ | 9.8 | 34 | >99 |
| 10[c] | 3.5 wt% $Ru/Co_3O_4$ | 9.8 | 7.7 | >99 |
| 11[c] | 10 wt% $Ru/Co_3O_4$ | 9.8 | 4.1 | >99 |
| 12[b] | 2.5 wt% $Ru/Co_3O_4$-*A* | 24.7 | 54 | >99 |

[a] Reaction conditions: benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K; time, 1 h. [b] Catalyst amount was fixed at 0.10 g. [c] Ru amount was fixed at 9.8 μmol by regulating the catalyst weight.

If the contact boundary between Ru species and $Co_3O_4$ particles plays a role in determining the catalytic activity, it can be expected that the size of $Co_3O_4$ will also affect the catalytic performances. The effect of size of oxide support on catalytic performances of supported catalysts has attracted much attention in recent years.[13,14] We exploited two $Co_3O_4$ samples ($Co_3O_4$ and $Co_3O_4$-*A* with surface areas of 26 and 5.6 $m^2$ $g^{-1}$, respectively) with different sizes for the preparation of supported ruthenium catalysts by the same adsorption-precipitation method. The BET surface areas of the 2.5 wt% $Ru/Co_3O_4$ and 2.5 wt% $Ru/Co_3O_4$-*A* were 32 and 13 $m^2$ $g^{-1}$, respectively. XRD patterns of the two $Co_3O_4$ samples and the two supported ruthenium catalysts are shown in Fig. 1. Only the diffraction peaks of crystalline $Co_3O_4$ with spinel structure were observed for these samples. No information about ruthenium species could be obtained possibly because the ruthenium species were in amorphous state or the Ru content was too low. Actually, any diffraction peaks assignable to Ru species could not be detected even for the $Ru/Co_3O_4$ catalyst with a Ru content of 10 wt%, indicating the amorphous state of ruthenium species in these catalysts. The diffraction peaks for the $Co_3O_4$ and the 2.5 wt% $Ru/Co_3O_4$ were significantly broader than those for the $Co_3O_4$-*A* and the 2.5 wt% $Ru/Co_3O_4$-*A*. Calculations using the Scherrer equation revealed that the sizes of $Co_3O_4$ and $Co_3O_4$-*A* were ~30 and ~100 nm, respectively, either before or after the loading of ruthenium species. SEM images shown in Fig. 2 for the 2.5 wt% $Ru/Co_3O_4$ and the 2.5 wt% $Ru/Co_3O_4$-*A* clearly revealed that the particle sizes of $Co_3O_4$ in the former catalyst were significantly smaller than those in the latter catalyst. We observed a significant difference in catalytic performance between these two catalysts (Table 4, entries 4 and 12). The $Ru/Co_3O_4$-*A* catalyst with larger $Co_3O_4$ particles exhibited a significantly lower conversion of benzyl amine (entry 12). It is reasonable to think that the smaller $Co_3O_4$ particles can lead to larger interfaces between the supported ruthenium species and the $Co_3O_4$ particles, and thus result in the higher catalytic performance of the $Ru/Co_3O_4$ catalyst. Thus, the present result further suggests that the interface between the Ru species and the $Co_3O_4$ particles plays a key role in determining the catalytic activity.

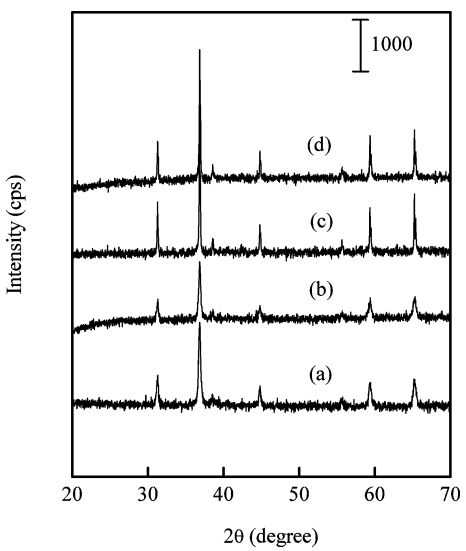



**Fig. 1** XRD patterns. (a) $Co_3O_4$, (b) 2.5 wt% $Ru/Co_3O_4$, (c) $Co_3O_4$-*A* and (d) 2.5 wt% $Ru/Co_3O_4$-*A*.

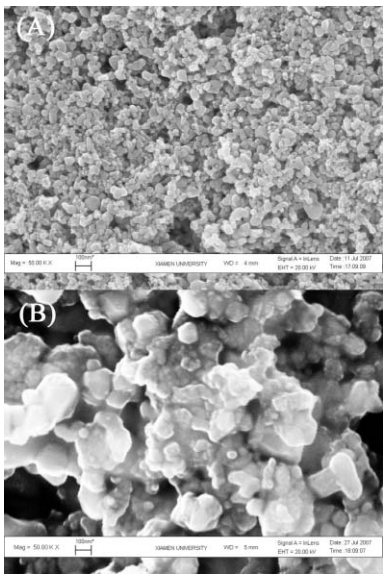



**Fig. 2** SEM images. (A) 2.5 wt% $Ru/Co_3O_4$, (B) 2.5 wt% $Ru/Co_3O_4$-*A*.

### Effects of kinetic factors on catalytic performances of $Ru/Co_3O_4$ catalyst for aerobic oxidation of benzyl amine

Fig. 3 shows the influence of the amount of catalyst on catalytic performances for the 2.5 wt% $Ru/Co_3O_4$ catalyst. Without a catalyst, benzyl amine conversion was almost zero. The conversion increased proportionally to the catalyst amount in the whole range investigated (0–0.10 g). These observations confirm that the catalyst plays essential roles in the aerobic oxidation of benzyl amine and the reaction proceeds steadily over the catalyst. The linear increase in benzyl amine conversion even at a higher conversion level may imply that the reaction rate is not strongly dependent on the concentration of the substrate.

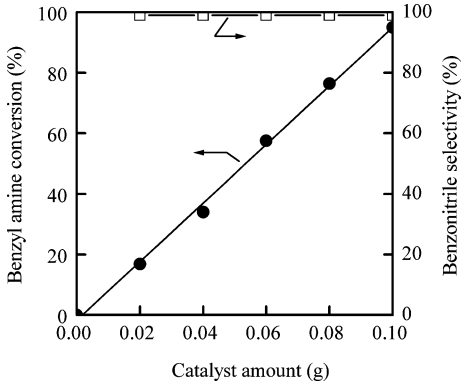



**Fig. 3** Effect of catalyst amount on catalytic performance of the 2.5 wt% $Ru/Co_3O_4$ for the aerobic oxidation of benzyl amine. Symbols: (●) benzyl amine conversion, (□) benzonitrile selectivity. Reaction conditions: benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K; time, 1 h.

The effect of reaction temperature on catalytic performance of the 2.5 wt% $Ru/Co_3O_4$ catalyst is shown in Fig. 4. Benzyl amine conversion increased exponentially with temperature. The activation energy calculated using the Arrhenius equation was 62 kJ $mol^{-1}$, further suggesting that the reaction was not rate-limited by the diffusion.

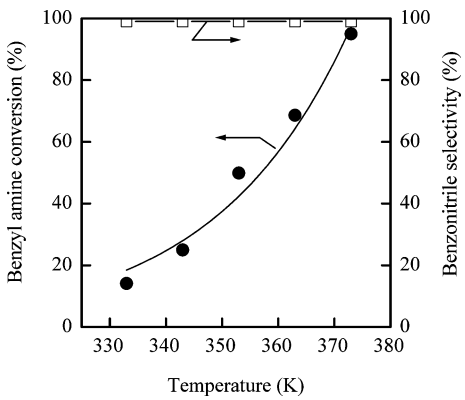



**Fig. 4** Effect of reaction temperature on catalytic performance of the 2.5 wt% $Ru/Co_3O_4$ for the aerobic oxidation of benzyl amine. Symbols: (●) benzyl amine conversion, (□) benzonitrile selectivity. Reaction conditions: catalyst, 0.1 g; benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; time, 1 h.

The time course plotted in Fig. 5 for the aerobic oxidation of benzyl amine over the 2.5 wt% $Ru/Co_3O_4$ catalyst at 353 K showed that the conversion increased linearly with time in the initial 0.5 h, and then the rate became slow. The initial conversion rate at 353 K was calculated to be 32 mol $h^{-1}$ mol-$Ru^{-1}$.

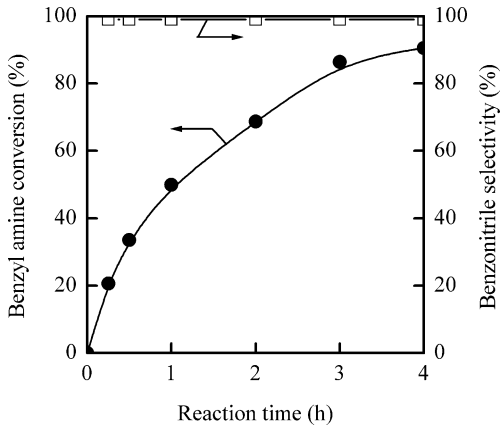



**Fig. 5** Time course for the aerobic oxidation of benzyl amine over the 2.5 wt% $Ru/Co_3O_4$ catalyst. Symbols: (●) benzyl amine conversion, (□) benzonitrile selectivity. Reaction conditions: catalyst, 0.1 g; benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 353 K.

The effect of oxygen pressure on catalytic performances at 353 K was investigated using ($O_2$+$N_2$) gas mixture instead of pure $O_2$ for the oxidation of benzyl amine over the 2.5 wt% $Ru/Co_3O_4$ catalyst. The result in Fig. 6 revealed that benzyl amine conversion did not change significantly with changing the partial pressure of oxygen in the range we investigated (0.2–1.0 atm). In other words, the reaction order with respect to oxygen was zero in this range. Thus, it is expected that air can also be used as an oxidant over our catalyst. Actually, using air (3 mL $min^{-1}$) instead of pure oxygen, the conversion of benzyl amine was 92% and the selectivity to benzonitrile was >99% over the 2.5 wt% $Ru/Co_3O_4$ catalyst under the reaction conditions shown in Table 2 (373 K).

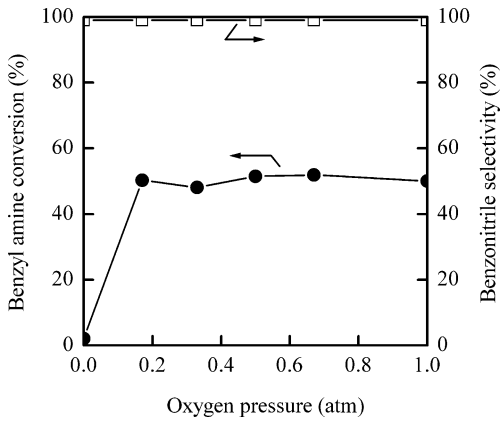



**Fig. 6** Effect of oxygen pressure on catalytic performance of the 2.5 wt% $Ru/Co_3O_4$ for the aerobic oxidation of benzyl amine. Symbols: (●) benzyl amine conversion, (□) benzonitrile selectivity. Reaction conditions: catalyst, 0.1 g; benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; ($O_2$ + $N_2$) flow rate, 6 mL $min^{-1}$; temperature, 353 K; time, 1 h.

Recycling uses of the 2.5 wt% $Ru/Co_3O_4$ catalyst for the aerobic oxidation of benzyl amine were investigated. The recovered catalyst after each run was washed with ethanol for

several times and then was reused in the next run after drying at ambient temperature. The result (Fig. 7) shows that the conversion of benzyl amine and the selectivity to benzonitrile are almost unchanged after repeated uses for 5 times. Therefore, the present $Ru/Co_3O_4$ catalyst is recyclable.

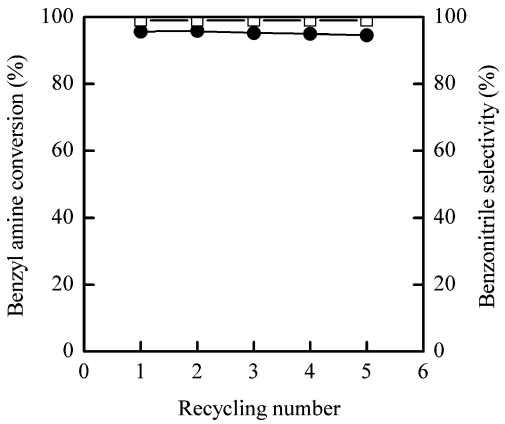



**Fig. 7** Recycling uses of the 2.5 wt% $Ru/Co_3O_4$ for the aerobic oxidation of benzyl amine. Symbols: (●) benzyl amine conversion, (□) benzonitrile selectivity. Reaction conditions: catalyst, 0.1 g; benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K; time, 1 h.

### $Ru/Co_3O_4$ catalyst for the aerobic oxidation of other amines and for the solvent-free aerobic oxidation of amines

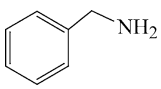
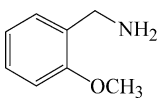
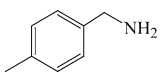
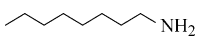
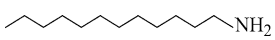
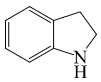
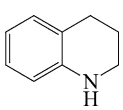
We applied the 2.5 wt% $Ru/Co_3O_4$ catalyst to the aerobic oxidation of several other amines. As summarized in Table 5, the substituted benzyl amines could also be selectively oxidized into the corresponding nitriles although the activity was slightly lower than benzyl amine. The oxidation of non-activated aliphatic amines also proceeded efficiently over the present catalyst (entries 4 and 5). Not only the primary amines, but also the heterocyclic amines were selectively oxidized in the presence of the $Ru/Co_3O_4$ catalyst. For example, indoline and 1,2,3,4-tetrahydroquinoline were oxidized selectively to indole and quinoline in good yields ($\geq$ 90%) after 2 and 6 h of reactions, respectively (entries 6 and 7).

It is highly desirable to perform solvent-free aerobic oxidation of amines from the viewpoint of green chemistry. We found that the 2.5 wt% $Ru/Co_3O_4$ catalyst was useful for the solvent-free aerobic oxidation of several kinds of amines (Table 6). Benzyl amine conversion and benzonitrile selectivity reached 91 and 98% after 24 h reaction at 423 K over our catalyst, giving a TON of 1829 $h^{-1}$ and a TOF of 76 $h^{-1}$. Other amines shown in Table 6 could also be selectively oxidized under solvent-free conditions. To the best of our knowledge, this is the first report on the solvent-free catalytic aerobic oxidation of amines. We have carried out recycling uses of the 2.5 wt% $Ru/Co_3O_4$ catalyst for the solvent-free aerobic oxidation of 1,2,3,4-tetrahydroquinoline. The catalyst could be recovered easily through centrifugation, and the conversion of 1,2,3,4-tetrahydroquinoline only decreased slightly after 4 reaction cycles (Table 6, entry 8).

### Insights into the state of ruthenium species active for aerobic oxidation of amines

To gain insights into the state of ruthenium species active for aerobic oxidation of amines, we have investigated the state-activity relationships using the catalysts deliberately prepared

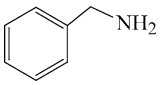
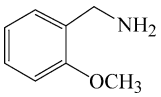
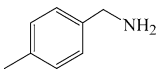
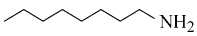
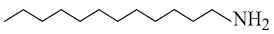
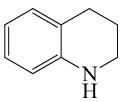
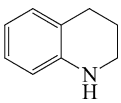
**Table 5** Aerobic oxidation of various amines catalyzed by the 2.5 wt% $Ru/Co_3O_4$ catalyst[a]

| Entry | Substrate | Time (h) | Conv. (%) | Select. (%) |
|---|---|---|---|---|
| 1 |  | 1 | 95 | >99 |
| 2 |  | 2 | 89 | >99 |
| 3 |  | 2 | 98 | >99 |
| 4 |  | 2 | 88 | >99 |
| 5 |  | 1 | 77 | >99 |
| 6 |  | 2 | >99 | >99 |
| 7 |  | 6 | 90 | >99 |

[a] Reaction conditions: amine, 1 mmol; catalyst, 0.10 g; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K.

**Table 6** Solvent-free aerobic oxidation of various amines catalyzed by the 2.5 wt% $Ru/Co_3O_4$ catalyst[a]

| Entry | Substrate | Temp. (K) | Time (h) | Conv. (%) | Select. (%) |
|---|---|---|---|---|---|
| 1 |  | 423 | 24 | 91 | 98 |
| 2 |  | 373 | 48 | 51 | >99 |
| 3 |  | 383 | 30 | 41 | >99 |
| 4 |  | 373 | 48 | 98 | >99 |
| 5 |  | 373 | 48 | 99 | >99 |
| 6 |  | 423 | 24 | 77 | >99 |
| 7 |  | 423 | 24 | 76 | >99 |
| 8[b] |  | 423 | 24 | 69 | >99 |

[a] Reaction conditions: amine, 50 mmol; catalyst, 0.10 g; $O_2$ flow rate, 3 mL $min^{-1}$. [b] Result after 4 recycles.

with different procedures as listed in Table 1. The catalysts were characterized by XRD, XPS and $H_2$-TPR techniques. From XRD measurements, we could not see significant differences among these catalysts. We only observed the diffraction peaks ascribed to $Co_3O_4$ (similar to those in Fig. 1), and no information about Ru species could be obtained possibly because of the lower content of Ru or the amorphous feature of the Ru species. Ru 3d XPS spectra of these catalysts are shown in Fig. 8. Generally, the

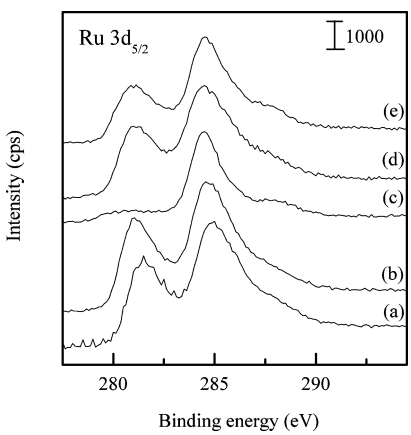



**Fig. 8** Ru 3d XPS spectra for the $Co_3O_4$-supported ruthenium catalysts prepared with different procedures. (a) 2.5 wt% $Ru/Co_3O_4$, (b) 2.5 wt% $Ru/Co_3O_4$-C573, (c) 2.5 wt% $Ru/Co_3O_4$-C573-R623, (d) 3 wt% $Ru/Co_3O_4$ (*imp*), (e) 3 wt% $Ru/Co_3O_4$ (*imp*)-C573.

C 1 s peak for carbon contamination at 284.6 eV was used as a reference for the correction of binding energy (BE). However, because of the overlapping of the peaks of Ru $3d_{3/2}$ and C 1 s, the Co $2p_{3/2}$ peak (BE, 779.5 eV) was used as a reference for our samples except for the 2.5 wt% $Ru/Co_3O_4$–C573-R623, for which the intensity of Ru $3d_{3/2}$ was very low and the peak position of C 1 s could be clearly discerned. The obtained BE of Ru $3d_{5/2}$ and the possible state of ruthenium species for each catalyst are summarized in Table 7. The BE of Ru $3d_{5/2}$ for the 2.5 wt% $Ru/Co_3O_4$ catalyst prepared by the adsorption-precipitation method was at 281.5 eV. The hydrous ruthenium oxide ($RuO_2 \cdot xH_2O$ or $RuO_xH_y$) was reported to exhibit a BE of Ru $3d_{5/2}$ at 281.4–281.8 eV,[15–17] which was higher than that for $RuO_2$ (280.7–281.0 eV)[18] owing to the presence of OH functional groups.[16] Thus, the XPS result suggests that the ruthenium species in the 2.5 wt% $Ru/Co_3O_4$ catalyst is in the hydrous $RuO_2$ state. The 2.5 wt% $Ru/Co_3O_4$-C573 possessed a lower BE of Ru $3d_{5/2}$ at 281.0 eV, indicating the transformation of $RuO_2 \cdot xH_2O$ to anhydrous $RuO_2$ species. The 2.5 wt% $Ru/Co_3O_4$-C573-R623 showed a much lower BE of Ru $3d_{5/2}$ at 280.0 eV, which could be assigned to metallic Ru.[18] For the 3 wt% $Ru/Co_3O_4$ (*imp*) and the 3 wt% $Ru/Co_3O_4$ (*imp*)-C573, the BE values of Ru $3d_{5/2}$ were both 280.9 eV. However, the surface molar ratio of Cl/Co estimated from XPS for the 3 wt% $Ru/Co_3O_4$ (*imp*) was significantly larger. The surface molar ratio of Cl/Ru for this sample was ~1.3. Thus, this sample might contain a mixture of $RuCl_3$ and $RuO_2$. This is consistent with some reported

**Table 7** XPS results for $Co_3O_4$-supported ruthenium catalysts prepared by different procedures

| Catalyst | BE of $Ru3d_{5/2}$ (eV) | Main state of Ru | Ru/Co[a] | Cl/Co[a] |
|---|---|---|---|---|
| 2.5 wt% $Ru/Co_3O_4$ | 281.5 | $RuO_2 \cdot xH_2O$ | 0.12 | 0.025 |
| 2.5 wt% $Ru/Co_3O_4$–C573 | 281.0 | $RuO_2$ | 0.11 | 0.022 |
| 2.5 wt% $Ru/Co_3O_4$–C573-R623 | 280.0 | Ru° | 0.02 | 0.020 |
| 3 wt% $Ru/Co_3O_4$ (*imp*) | 280.9 | $RuCl_3$ and $RuO_2$ | 0.13 | 0.17 |
| 3 wt% $Ru/Co_3O_4$ (*imp*)–C573 | 280.9 | $RuO_2$ | 0.09 | 0.014 |

[a] Molar ratio calculated from XPS analysis.

results that $RuCl_3$ is not stable and may easily be converted to $RuO_2$ by heating in air, and that even some commercial $RuCl_3$ comprises ruthenium species with higher valence states.[15,19,20] After calcination, the 3 wt% $Ru/Co_3O_4$ (*imp*)-C573 sample exhibited a lower ratio of Cl/Co, indicating that $RuO_2$ became the main ruthenium species. The surface Cl/Co molar ratios for the series of samples prepared by the adsorption-precipitation method were also quite low, confirming that only a small amount of Cl remained in these samples. Table 7 also shows that the surface molar ratios of Ru/Co for these samples (except for the 2.5 wt% $Ru/Co_3O_4$-C573-R623) are similar (0.09–0.13). These values of Ru/Co molar ratio are larger than that expected from the bulk composition (~0.02). Thus, the ruthenium species are probably located on the surface of $Co_3O_4$ in these samples except for the 2.5 wt% $Ru/Co_3O_4$-C573-R623.

Fig. 9 shows $H_2$-TPR profiles for the $Co_3O_4$-supported ruthenium catalysts prepared by different procedures. $Co_3O_4$ alone showed two reduction peaks at 588 and 696 K, and the quantitative calculations suggested that these two peaks likely corresponded to the reductions of $Co^{III}$ to $Co^{II}$ and $Co^{II}$ to Co°, respectively. The hydrous ruthenium oxide ($RuO_2 \cdot xH_2O$) exhibited a single reduction peak at 430 K, corresponding to the reduction of $Ru^{IV}$ to Ru°. The 2.5 wt% $Ru/Co_3O_4$ catalyst exhibited two reduction peaks at 403 and 564 K (curve b). The quantification suggested that the lower-temperature peak could not be assigned only to the reduction of Ru species from +IV to 0, and it must also comprise the reduction of $Co_3O_4$. The calculation implied that the lower-temperature peak comprised the reduction of $Co^{III}$ to $Co^{II}$ in addition to $Ru^{IV}$ to Ru°, and the higher-temperature peak corresponded to the reduction of $Co^{II}$ to Co°. Thus, the loading of Ru species on $Co_3O_4$ significantly enhanced the reduction of $Co_3O_4$. The same phenomenon was also observed for the Ru-Co binary oxides prepared by a co-precipitation method.[21] As compared with the 2.5 wt% $Ru/Co_3O_4$, the reduction peaks for the 2.5 wt% $Ru/Co_3O_4$-C573 (curve c) and the 3.0 wt% $Ru/Co_3O_4$ (*imp*)-C573 (curve d) shifted significantly to higher temperatures. Combined with the information from XPS measurements described above, this result suggests that the $Co_3O_4$-supported hydrous $RuO_2$ possesses higher reducibility than the supported anhydrous $RuO_2$.

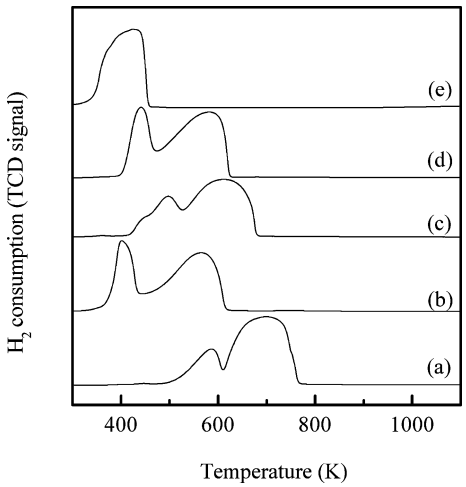



**Fig. 9** $H_2$-TPR profiles for the $Co_3O_4$-supported ruthenium catalysts prepared with different procedures together with $Co_3O_4$ and hydrous $RuO_2$. (a) $Co_3O_4$, (b) 2.5 wt% $Ru/Co_3O_4$, (c) 2.5 wt% $Ru/Co_3O_4$-C573, (d) 3 wt% $Ru/Co_3O_4$ (*imp*)-C573, (e) $RuO_2 \cdot xH_2O$.

The catalytic performances of these catalysts as well as the single $Co_3O_4$ and $RuO_2 \cdot xH_2O$ for the aerobic oxidation of benzyl amine are summarized in Table 8. The single $RuO_2 \cdot xH_2O$ showed a very low conversion under the reaction conditions of Table 8, indicating that the dispersion of $RuO_2 \cdot xH_2O$ on a support played a key role in enhancing its catalytic performance. The $Ru/Co_3O_4$ (*imp*) without calcination showed a conversion comparable to that of $Co_3O_4$ alone (entry 3). Moreover, we

**Table 8** Catalytic behaviours of $Co_3O_4$-supported ruthenium catalysts with ruthenium in different states for aerobic oxidation of benzyl amine to benzonitrile[a]

| Entry | Catalyst | Ru amount (μmol) | Conv. (%) | Select. (%) |
|---|---|---|---|---|
| 1 | $Co_3O_4$ | — | 2.0 | >99 |
| 2 | $RuO_2 \cdot xH_2O$ | 29.7 | 1.2 | >99 |
| 3 | 3 wt% $Ru/Co_3O_4$ (*imp*) | 29.7 | 1.8 | >99 |
| 4 | 3 wt% $Ru/Co_3O_4$ (*imp*)-C573 | 29.7 | 14 | >99 |
| 5 | 2.5 wt% $Ru/Co_3O_4$ | 24.7 | 95 | >99 |
| 6 | 2.5 wt% $Ru/Co_3O_4$–C573 | 24.7 | 19 | >99 |
| 7 | 2.5 wt% $Ru/Co_3O_4$–C573-R623 | 24.7 | 0.9 | >99 |

[a] Reaction conditions: benzyl amine, 1 mmol; solvent ($PhCF_3$), 5 mL; $O_2$ flow rate, 3 mL $min^{-1}$; temperature, 373 K; time, 1 h.

confirmed that the homogeneous oxidation of benzyl amine by $O_2$ using $RuCl_3$ catalyst could not occur under our reaction conditions. Thus, the supported $RuCl_3$ species should not be the active species. On the other hand, the catalyst prepared by the adsorption-precipitation method without calcination exhibited a significantly higher activity (entry 5). Thus, the supported hydrous $RuO_2$ was a highly efficient species for the aerobic oxidation of amines. The conversion of benzyl amine over the calcined 2.5 wt% $Ru/Co_3O_4$–C573 became remarkably lower (entry 6). The 3 wt% $RuO_x/Co_3O_4$ (*imp*)-C573 exhibited a similar activity (entry 4) to the 2.5 wt% $Ru/Co_3O_4$–C573. These observations further confirm that the ruthenium species in these two catalysts are the same (i.e., anhydrous $RuO_2$). Thus, the supported anhydrous $RuO_2$ possesses a lower activity in the aerobic oxidation of benzyl amine. The result in Table 8 also suggests that the metallic Ru species cannot catalyse the aerobic oxidation of amines because the 2.5 wt% $Ru/Co_3O_4$–C573-R623 is almost inactive (entry 7).

Because the heterogeneous catalysts reported for the aerobic oxidation of amines are still scarce,[7,8,11] the insights into the active sites are very limited. Kaneda and co-workers suggested that a monomeric $Ru^{III}$ with Cl ligands attached on hydroxyapatite was responsible for the selective oxidation of amines.[7,22] Yamaguchi and Mizuno proposed $Ru(OH)_3$ as the active species for their $Ru/Al_2O_3$ catalyst.[8] Our results described above have revealed that the $Co_3O_4$-supported hydrous $RuO_2$ is the active species for the aerobic oxidation of amines. The supported anhydrous $RuO_2$ only showed a lower activity. The metallic Ru (Ru°) or the $RuCl_3$ species were inactive for the aerobic oxidation of amines. It is of interest to note that the hydrous $RuO_2$ with or without a support has been reported to be an active phase for the aerobic oxidation of alcohols by a few groups.[21,23–25] EXAFS studies showed that the hydrous $RuO_2$ possesses a two-dimensional structure of independent chains, in which $RuO_6$ octahedra are connected by two shared oxygen atoms, and the $RuO_6$ octahedra contain Ru-OH or Ru-$OH_2$ bonds of ~2.5 Å.[25,26] With reference to the reaction mechanism proposed for the aerobic oxidation of alcohols over the hydrous $RuO_2$ species,[21] we consider that the Ru-OH or Ru-$OH_2$ bond may be transformed into Ru-$NHCH_2R$ *via* the interaction with $RNH_2$ as follows,

$$Ru^{IV}\text{-}OH + RCH_2NH_2 \rightarrow Ru^{IV}\text{-}NHCH_2R + H_2O.$$

The $Ru^{IV}$-$NHCH_2R$ may undergo β-hydrogen elimination to give imine, which would be further oxidized and transformed into nitrile.[8] Whether the redox of $Ru^{IV}/Ru^{III}$ occurs during the reaction or the $Ru^{IV}$ only acts as a Lewis acid still remains unclear. Our $H_2$-TPR result (Fig. 9) showed that the supported hydrous $RuO_2$ could be reduced at a significantly lower temperature than the supported anhydrous $RuO_2$. The higher reducibility of the hydrous $RuO_2$ species might contribute to its higher catalytic activity. It is well known that hydrous $RuO_2$ is a mixed electron-proton conductor.[26] We speculate that the proton-conducting property of the hydrous $RuO_2$ may be beneficial to the β-hydrogen elimination, which might be the rate-determining step.

Because $RuO_2{\cdot}xH_2O$ alone only exhibits a lower activity in the aerobic oxidation of benzyl amine, the synergistic effect between $RuO_2{\cdot}xH_2O$ and $Co_3O_4$ is very significant. The results of effects of Ru loadings and $Co_3O_4$ sizes on catalytic performances (Table 4) suggest that the contact boundary between the amorphous $RuO_2{\cdot}xH_2O$ and the $Co_3O_4$ particles really plays a key role in enhancing the catalytic activity. The synergistic effect between $Ru^{IV}$ and $Co^{III}$ or $Co^{II}$ has also been observed for a few catalysts effective for the aerobic oxidation of alcohols such as the Ru–Co binary oxide catalyst prepared by the co-precipitation method.[21,24] and the Ru–Co–Al hydrotalcite catalyst[27] The role of Co was proposed to facilitate the catalyst regeneration by removing the hydrogen (hydride species) attached on Ru sites over the Ru–Co binary oxide for alcohol oxidation.[21] We speculate that, in our case, the Co sites may play a similar role. In our case, $Co^{II}$ may participate in the activation of $O_2$ to reoxidise the reduced $Ru^{III}$ species if the redox of $Ru^{IV}/Ru^{III}$ exists or to remove the hydride species to regenerate the Ru sites.

## Conclusions

The $Co_3O_4$-supported ruthenium catalyst was found to exhibit the best catalytic performance for the aerobic oxidation of benzyl amine among various metal oxide-supported ruthenium catalysts and $Co_3O_4$-supported various transition metal catalysts prepared by an adsorption-precipitation method. The increase in ruthenium loadings to ≥ 3.5 wt% significantly decreased the catalytic activity. The size of $Co_3O_4$ particles affected the performance of the supported ruthenium catalyst, and the smaller size of $Co_3O_4$ led to the higher catalytic activity. The catalytic activity was strongly dominated by the state of ruthenium species. While the supported anhydrous ruthenium oxide only exhibited a lower activity, the hydrous ruthenium oxide dispersed on $Co_3O_4$ showed remarkably higher efficiency for the aerobic oxidation of benzyl amine. The supported metallic ruthenium and ruthenium chloride species were inactive. The present $Co_3O_4$-supported hydrous ruthenium oxide catalyst was also effective for the aerobic oxidation of several other amines and could be used recyclably. The catalyst could be operated under solvent-free conditions or using air instead of oxygen as an oxidant.

## Acknowledgements

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